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A STUDY OF THE GAS PHASE GAMMA
RADIOLYSIS OF MONOMETHYLAMINE
AND DEUTERATED MONOMETHYLAMINES.**

**University of New Hampshire, Ph.D., 1966
Chemistry, physical**

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A STUDY OF THE GAS PHASE GAMMA RADIOLYSIS
OF
MONOMETHYLAMINE AND DEUTERATED MONOMETHYLAMINES

BY

GEORGE EDWARD McALONIE

B. S., State University of New York College
at Albany, 1960

A THESIS

Submitted to the University of New Hampshire
In Partial Fulfillment of
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Doctor of Philosophy

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This thesis has been examined and approved.

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James D. Morrison

Francis R. Hall

David W. Ellis

Gloria D. Kyle

August 25, 1965

Date

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George E. McAlonie

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INTRODUCTION

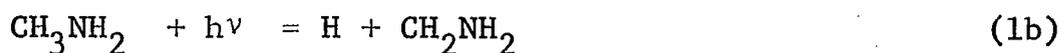
Previous work¹ in this laboratory has been concerned with the isolation and determination of the products of the gas phase gamma radiolysis of methylamine, ammonia, dimethylamine, and trimethylamine. As a result of this work mechanisms of product formation were proposed, but it was felt that more intensive studies should be made using deuterium labelled compounds as an aid to elucidate the proposed mechanisms.

This thesis is a study of the gamma radiolysis of monomethylamine, monomethylamine-d₂ and monomethyl-d₃-amine-d₂, and certain mixtures of these in the gas phase.

The utility of the use of deuterium labelled compounds was realized in the work of Dorfman² where it was shown that a gaseous mixture of C₂H₆-C₂D₆-scavenger yielded primarily H₂ and D₂ upon radiolysis with 1.5 Mev electrons. Okabe and McNesby³ irradiated ethane, especially CH₃CD₃, with 1470 and 1295 Å xenon radiation and showed that the major product, hydrogen, is formed intramolecularly and preferentially from the same carbon atom. A study of CH₃CD₃ by Stief and Ausloos⁴ using a cobalt 60 gamma source also led to the conclusion that the intramolecular formation of hydrogen is an important process, but elimination of a hydrogen molecule from the same carbon atom does not necessarily hold for radiolysis. These findings are quite significant when one considers that prior thinking on the primary processes in these fields was based on the intermolecular formation of hydrogen.⁵

Monomethylamine has been subjected to thermal and photochemical studies.⁶ In the work by Michael and Noyes⁷ the photo-

lysis of CH_3NH_2 , CD_3NH_2 and CH_3ND_2 separately with U.V. light (1940 to 2440 Å) was studied at room temperature. This photolysis yielded hydrogen, ammonia, ethylenimine and dimethylamine as the major products; methane, ethane, nitrogen and azomethane were formed to a lesser extent. A polymer was also produced, but could not be characterized. The authors considered the primary dissociations to be



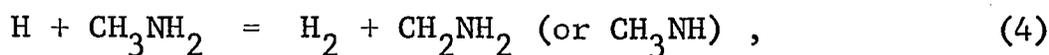
Isotopic analysis by mass spectrometry of the hydrogen formed from CD_3NH_2 showed about equal amounts of H_2 and HD were produced, with very little D_2 . The methane contained CD_3H as the major component, with CD_4 and a trace of CD_2H_2 . The ethane was mostly C_2D_6 with some $\text{C}_2\text{D}_5\text{H}$. With CH_3ND_2 the hydrogen was mainly HD while much more H_2 was present than D_2 . The methane yielded approximately equal amounts of CD_4 and CD_3H , the ethane was completely C_2H_6 .

The authors concluded that reaction (1a) must account for at least 75% of the primary process and estimated that reaction (1b) is 10% of (1a). They also noted that hydrogen atom abstraction from the CH_3 seems to be preferred over that from ND_2 in CH_3ND_2 .

Reaction (1c) accounted for the formation of methane and ethane according to



Further, reactions (1a) and (1b) were said to be followed by



where the ammonia producing reaction would then involve two radicals of the empirical formula CNH_4 ,



C_2NH_5 is the empirical formula of ethylenimine. It was noted that dimethylamine and nitrogen were formed by reactions which were difficult to elucidate.

Earlier, Watson and Darwent^{6h} had studied the photochemical decomposition of CH_3ND_2 and CD_3NH_2 separately. Their results of hydrogen isotope analysis agree qualitatively with those of Michael and Noyes since the former investigators stated that they were working with compounds of questionable isotopic purity. In both works, essentially the same mechanisms were postulated. In neither study were mixtures of monomethylamine and monomethyl- d_3 -amine- d_2 used in an attempt to clarify the possible primary processes.

Schiek has investigated the radiolysis of monomethylamine.¹ The decomposition by cobalt 60 gamma radiation (photons of 1.17 Mev and 1.33 Mev energy) resulted in hydrogen, ammonia and dimethylamine as the major products; methane was formed to a lesser extent. No other products, including a polymer, were detected. The dimethylamine initially reached a high concentration then decreased with irradiation time.

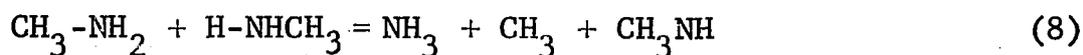
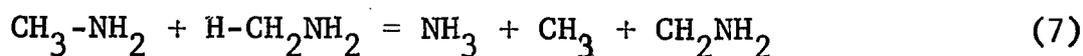
The author proposed



as the main step in hydrogen formation, based on the work of Watson and Darwent.^{6h}

Since ammonia production was dependent on pressure,

the data suggested a bimolecular reaction.

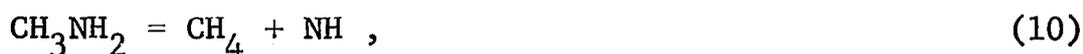


It was noted that reaction (8) could account for dimethylamine formation. The reaction



was also considered plausible.

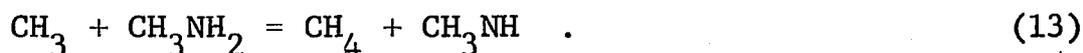
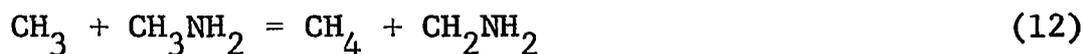
Methane formation was rationalized by several paths.



or carbon-nitrogen bond scission



followed by



Addition of iodine decreased the yield of ammonia and dimethylamine, indicating that free radical reactions may be operative. Charge transfer reactions were also demonstrated since addition of helium and argon increased the yield of ammonia.

EXPERIMENTAL

A. Chemicals

1. Monomethylamine (CH_3NH_2)

Anhydrous monomethylamine was obtained from the Matheson Company, Rutherford, New Jersey. The stated purity was 99.8 mole %; analysis by gas chromatography showed impurities of ammonia, dimethylamine and trimethylamine. After bleeding the gas into the vacuum line, a center cut was taken and distilled from a bath at -85°C (dry ice - trichloroethylene) to a receiver at -196°C (liquid nitrogen). This was followed by two hours of pumping on the solid methylamine held at -130°C (melting n-propyl alcohol bath). At fifteen minute intervals the solid was allowed to thaw and then re-frozen. After the operations, the gas was distilled into a storage bulb. Using gas chromatography, it was noted that the procedure removed most of the ammonia and trimethylamine with dimethylamine remaining as the major impurity. The infrared spectrum agreed very well with that of Gray and Lord.⁸

2. Monomethylamine- d_2 (CH_3ND_2)

The method of Gray and Lord⁸ was used with some modifications. Methylamine hydrochloride (Matheson, Coleman and Bell, Lot No. 381086) was recrystallized from water three times and dried in a drying pistol. Nine grams of the methylamine hydrochloride were placed in a 50 ml. long-necked flask, fitted with a 19/38 standard taper female joint. Fifteen grams of D_2O (99.8 mole % of D_2O from Bio-Rad Laboratories, Richmond, California) were then added and the mixture refluxed

for 4 hrs. The spent D_2O was distilled off under vacuum at room temperature after the exchange. Fresh D_2O was then added to the salt and the refluxing and distilling were repeated three more times. The final distillation removed only about one-half of the spent D_2O . After the final exchange and distillation to one-half volume, CaO , which had been heated to $450^\circ C$ under a running vacuum for two days to remove $Ca(OH)_2$, was added to the solution in the flask. The flask was attached to the vacuum line and evacuated. Monomethylamine- d_2 was generated by placing an air bath around the flask and heating to $200^\circ C$. The gas was condensed in a U trap immersed in liquid nitrogen. The solid was then pumped on for 15 min. By replacing the liquid nitrogen bath with a dry ice-trichloroethylene bath and placing the liquid nitrogen at the storage bulb, the gas was distilled into the storage bulb.

Infra-red analysis showed the chemical purity of monomethylamine to be at least 98 mole %. The slight perceptibility of the strong methylamine- d_1 band at 878 cm.^{-1} indicated that isotopic purity was at least 95 mole % of CH_3ND_2 .

3. Monomethyl- d_3 -amine- d_2 (CD_3ND_2)

The synthesis of completely deuterated methylamine involved the preparation of methyl- d_3 bromide after the method of Nolin and Leitch⁹, the preparation of methyl- d_3 -amine hydrochloride starting with CD_3Br as described by Cox and Warne¹⁰ and modified by Gray and Lord⁸, complete deuteration as cited above for methylamine- d_2 deuteriochloride, and finally, generation of the free amine by the same procedure. Since modifications were implemented by the author, the preparative scheme is outlined for purposes of clarity.

a. Twenty-eight grams of malonic acid (Fisher Chemical Co., Reagent grade, Lot No. 734681) were exchanged for 2

hrs. at room temperature with 29 grams of D_2O (Bio-Rad Laboratories, 99.8 mole % of D_2O) in a 100 ml. flask fitted with a 19/38 standard taper female joint. The spent D_2O was distilled off with a Rinco apparatus under running vacuum and collected in a dry ice-acetone trap. Fresh D_2O was then added to the malonic acid and the procedure repeated five more times. After the final batch of spent D_2O was removed, the acid was dried on a vacuum line overnight.

b. The malonic acid- d_4 was decarboxylated and the acetic acid- d_4 distilled using an all-glass distillation head attached to the 100 ml. flask through a standard taper joint.

c. The acetic acid- d_4 was diluted with cold water and neutralized with cold 6N ammonium hydroxide. A slight excess of 3N silver nitrate was added with stirring and the silver acetate- d_3 was precipitated and dried in a vacuum desiccator, stored in the dark, for thirty-six hours.

d. The dried silver acetate- d_3 was reacted with dry bromine (Baker Analyzed Reagent) at room temperature in a vacuum line (operating pressure, 10^{-3} mm. Hg). The acetate was loosely packed at the top of an ascarite column (approx. 46 cm. long), a receiving flask was attached to the bottom of the column by a 12/30 standard taper joint. The methyl- d_3 bromide was trapped in this flask with liquid nitrogen. Twenty-seven grams of dried silver acetate- d_3 were divided into five batches and each batch was run separately with fresh ascarite. Great care had to be taken when passing the bromine over the acetate since the reaction is very exothermic.

e. The methyl- d_3 bromide was passed through phosphorous pentoxide and ascarite in turn to remove any impurities remaining, and was frozen into the side arm of a 100 ml. flask containing a stoichiometric amount of potassium phthali-

amide (Kodak White Label, Lot No. 37A) which had been pumped on at 180°C for 1 hr. to remove any water. The flask was then sealed off. The main body of the flask was placed in an air bath at 130°C; the side arm was at room temperature. The reaction was allowed to proceed under these conditions for 12 hrs.

The flask was opened and the solid scrapped out, washed twice with cold water, three times with cold 1N potassium hydroxide, and three times with cold water. The N-methyl-d₃ phthalimide was dried in a vacuum desiccator and then extracted with carbon disulfide in a Soxhlet extraction apparatus. The carbon disulfide was removed on a Rinco.

f. The N-methyl-d₃ phthalimide was refluxed with constant boiling hydrochloric acid for 30 hrs. After cooling, the precipitated phthalic acid was filtered off and the remaining solution evaporated on a Rinco. The weight of the dried monomethyl-d₃-amine hydrochloride was 2.06 grams.

g. The monomethyl-d₃-amine hydrochloride was refluxed with batches of 6 grams of D₂O (Bio-Rad Laboratories, 99.8 mole % D₂O) and generated in the same manner as in the preparation of monomethylamine-d₂.

Infra-red spectra showed the chemical purity of the amine to be at least 98 mole %. NMR and infra-red studies indicated the isotopic purity to be approximately 95 mole % in CD₃ND₂; 5 mole %, CHD₂NHD.

B. Apparatus and Equipment

1. Cobalt-60 Source

The construction and operation of the 85 curie (September, 1962) source has been previously described.¹¹ The strength of the source with respect to each irradiation position was calibrated.

2. Vacuum System

A drawing of the vacuum line used in the work is shown in Figure I. The entire system was fabricated from Pyrex brand glass except for the vacuum rubber tubing between the mechanical forepump (Welch Duo-Seal type) and the oil back-up trap bulb. Irradiation ampoules, Toepler pump and any accessories were attached to the main manifold through the 10/30 joints.

3. Toepler Pump

Figure II-a shows the Toepler pump used to separate the non-condensable product gases at -160°C from the condensables of the irradiated sample. The righthand, three-way stopcock was connected to the main manifold by a piece of heavy walled tygon tubing, Pyrex glass tubing and a standard taper male joint.

4. Irradiation Ampoules

The irradiation ampoules shown in Figure II-b were made by fusing a piece of 10 mm. O.D. Pyrex tubing to a length of 2 mm. I.D. capillary Pyrex tubing fitted with a 10/30 standard taper male joint. The ampoule was then fashioned by drawing out the 10 mm. tubing to a break seal so that the main body, excluding break seal and capillary, measured 8 to 8.5 cm. in length. Some irradiation vessels were 5 to 5.5 cm. in length. Care was always taken in checking each ampoule for leaks.

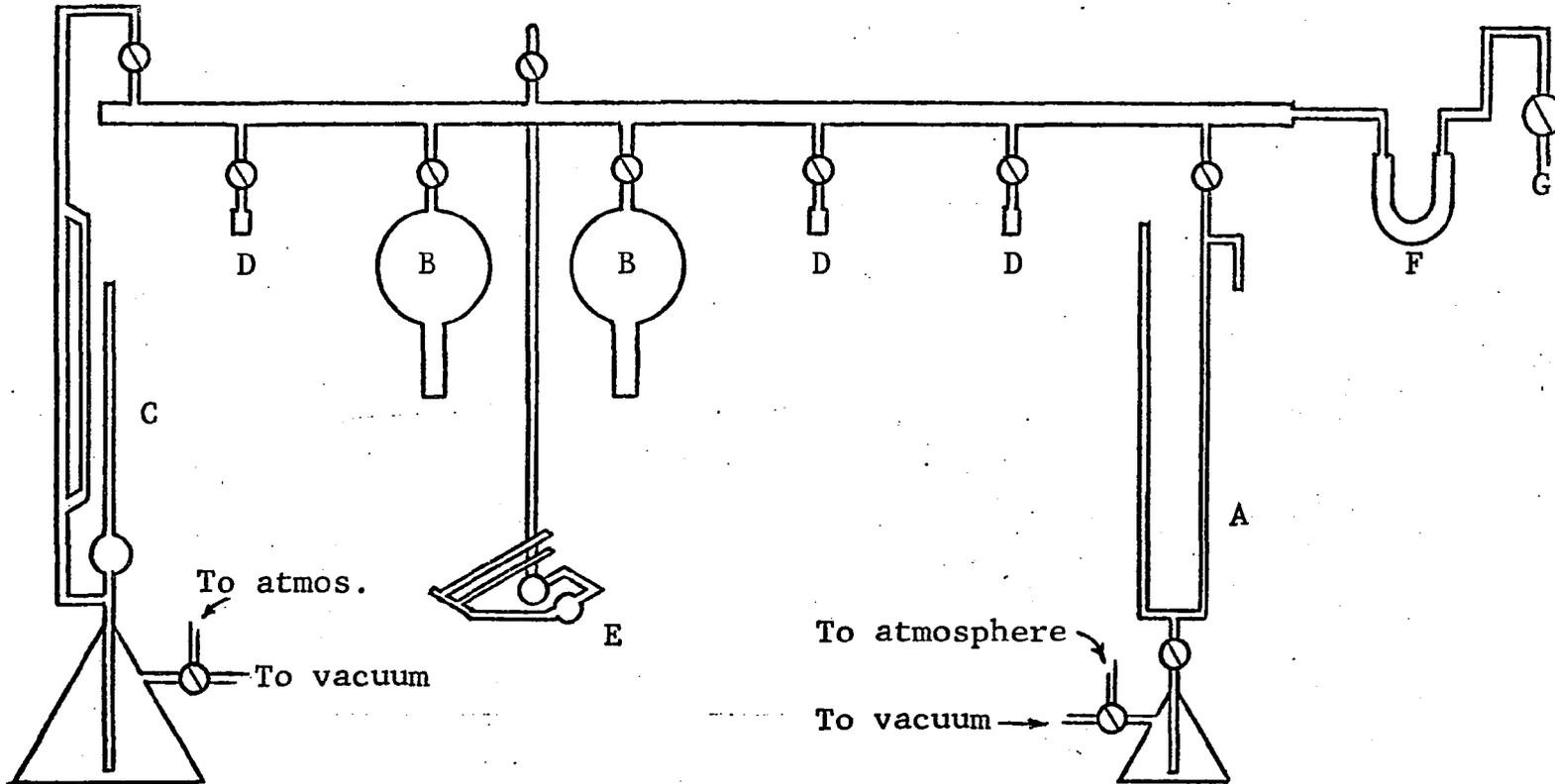
5. Infra-red Spectrophotometer

All spectra of the gases were run on a Perkin-Elmer grating IR Spectrophotometer, Model 337. The optics for the 10 cm. gas cell were NaCl.

6. NMR

A Varian, Model A-60, nuclear magnetic resonance spectrometer was used to check the isotopic purity of the malonic

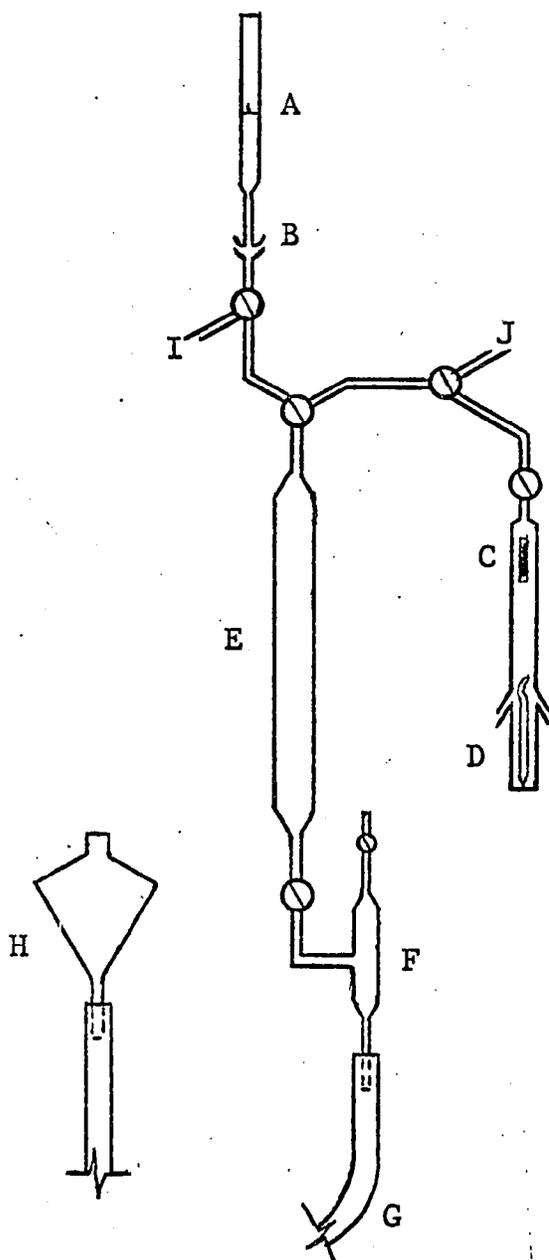
FIG. I - Vacuum Line



⊙ - stopcock
 A - gas burette
 B - storage bulb
 C - standing McLeod gauge

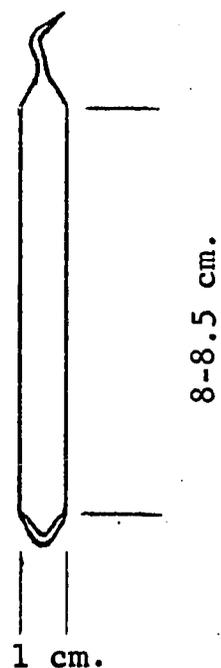
D - 10/30 joint
 E - tilting McLeod gauge
 F - U trap
 G - To traps, mercury diffusion pump
 and forepump

FIG. II-a



Toepler Pump

FIG. II-b



Irradiation Ampoule

- ⊙- stopcock
- A-Corning type break-seal
- B-12/5 ball joint
- C-glass enclosed nail
- D-irradiation ampoule
- E-mercury piston
- F-air trap
- G-tygon tubing
- H-leveling bulb
- I-to atmosphere
- J-to vacuum line

acid after the final exchange with D_2O . The solvent used was also D_2O for both the deuterated and the non-deuterated malonic acid.

7. Gas Chromatograph

A diethanolamine, lauryl alcohol, sodium iodide on Fluoropak 80 column¹² was used in a Perkin-Elmer, Model 154B, Vapor Fractometer.

C. Procedures

1. Preparation of Samples

The irradiation ampoule was attached to the vacuum line by a 10/30 standard taper joint and pumped on while checking for leaks with a Tesla coil. After pumping at a pressure of 10^{-4} mm. Hg, or less, for ten to fifteen minutes, the main stopcock was closed and after a period of ten minutes the pressure was read. If the pressure was less than 10^{-3} mm. Hg, it was taken as an indication that there were no leaks; the slight increase in pressure was due to air still absorbed in the freshly applied stopcock grease. This was proven to be the case in blank runs.

The main stopcock was again opened and pumping was continued for twenty to thirty minutes on the whole line including the gas burette, flaming the line at regular intervals. The pressure was again checked. The main stopcock and all others were closed. The burette stopcock was opened and gas from a storage bulb bled slowly into the burette until the desired pressure was reached. The burette stopcock was then closed. Liquid nitrogen was placed at the storage bulb. Twenty minutes were usually required for all the gas in the line to be frozen back into the bulb after which the bulb stopcock was closed. Liquid nitrogen was placed at the cold finger of the gas burette and the gas frozen. The burette stopcock was then opened for a count of ten to freeze into the cold

finger any gas in the stopcock bore. The burette stopcock was closed, the liquid nitrogen removed, and the gas allowed to come to thermal equilibrium (ten to fifteen minutes) with hand warming of the cold finger. While equilibrium was being reached in the gas burette, the stopcock to the ampoule was opened along with the main stopcock and the ampoule pumped on. After thermal equilibrium was attained in the burette, the main stopcock was closed, a liquid nitrogen bath was placed around the ampoule, and the burette was then opened to the irradiation vessel. Following the initial surge of gas from the burette, the burette stopcock was closed and then opened only five times for a count of ten in an interval of twenty minutes. From control samples, it was found that this yielded quantitative transfer and prevented large amounts of mercury from entering the ampoule. Finally, the stopcock to the ampoule was closed and the vessel was sealed off at the capillary while the liquid nitrogen bath remained in place.

2. Addition of Argon to Samples

When argon (Matheson Co., 99.9 mole %) was added to a given sample, the methylamine was frozen into the ampoule by the same procedure as given above except that in the final step the stopcock to the irradiation ampoule was closed, but the ampoule was not sealed off until the argon had been added.

An argon storage bulb was connected to the main manifold through a 10/30 standard taper joint and the line pumped down to 10^{-4} mm. Hg. A liquid nitrogen bath was placed at the argon storage bulb and its stopcock was opened for one minute, then closed. With another liquid nitrogen bath at the ampoule, the ampoule stopcock was opened for fifteen seconds, then closed. The process was repeated two more times and then the ampoule was sealed off. This procedure insured that argon was present in the sample at approximately 130 mm. Hg

pressure, the vapor pressure of solid argon at -196°C .

3. Separation of Products from Irradiated Samples

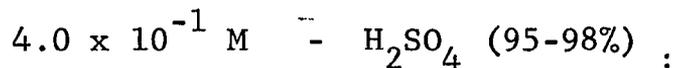
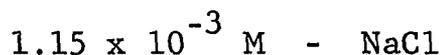
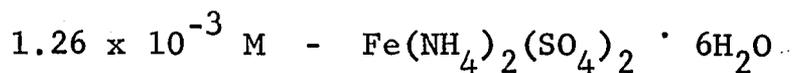
The separation of the non-condensable gases from the condensable gases, at -160°C , of the irradiated samples was effected with a Toepler pump. The irradiation ampoule was placed in the appropriate compartment, the Corning type, break seal tube was attached by capillary tubing and a ball joint connection to the upper lefthand stopcock, and the whole system was evacuated. Care was taken to check the break seal for leaks. Each section of the system was flamed gently. Because of the piece of heavy walled tygon tubing used as part of the connection to the main manifold, the pressure obtainable was slightly less than 10^{-3} mm. Hg.

When all sections were evacuated, the righthand three-way stopcock was turned so that it connected the ampoule breaking chamber with the mercury piston. Stopcocks to the chamber itself and to the break seal were closed. The ampoule was broken by allowing a glass enclosed nail to drop on it; a bath of liquid nitrogen was placed at the chamber for two minutes and then replaced with a melting iso-pentane bath. After an interval of ten minutes, the toeplerization was begun. Following the final toeplerization, the mercury was forced up into the capillary about a quarter of an inch from a constriction just below the capillary-break seal fuse joint. The break seal tube containing the non-condensable gases was then sealed off. A small amount of the non-condensables was lost by this method, but it proved efficient.

The bath was removed from the ampoule chamber and the remaining (non-condensable) gases were frozen into another break seal apparatus which had been previously attached to the main manifold. This vessel was then sealed off.

4. Cobalt 60 Source

The gamma ray source was calibrated for each position with a Fricke dosimeter solution,



5 ml. each of the solution were pipetted into tubes which resembled the irradiation ampoules. For every run, eight of the filled tubes were placed in appropriate positions around the interior of the holder used to secure the ampoules during irradiation. The position of the holder, and therefore the samples, could never be exactly duplicated either during sample irradiations or calibration runs. The solutions were exposed to the gamma rays for a given time interval in each run and their optical density was determined at 26.5°C with a Beckman DU spectrophotometer equipped with 1 cm. quartz cells, the unirradiated solution serving as a reference. Using the value of 2201 liter mole⁻¹ cm.⁻¹ at 25°C for the extinction coefficient of Fe⁺³ at 305 mμ given by Allen¹³, the concentration of the Fe⁺³ ion and the dose rate were calculated for each position. Since the extinction coefficient has a temperature coefficient of +0.7 % deg. C⁻¹, the dose rate was corrected accordingly.

Position Number	Dose Rate - $\text{ev gm.}^{-1} \text{ min.}^{-1}$
1	9.1×10^{16}
2	7.9×10^{16}
3	7.9×10^{16}
4	8.0×10^{16}
5	9.1×10^{16}
6	10.2×10^{16}
7	11.0×10^{16}
8	10.2×10^{16}

For gases, the dose rate must be further corrected by a factor of the ratio of the electron density of methylamine to that of water, 1.04.

D. Mass Spectrometer Analysis

The non-condensable gases, at -160°C , from the radiation of monomethylamine- d_2 (MAd_2) were analyzed by F. M. Roberts of Texaco, Inc., Beacon, New York, using a Consolidated Electrodynamic Corporation Model 12-103C mass spectrometer at an ionizing voltage of 70 volts. The non-condensable gases from the irradiation of equal and non-equal mole mixtures of monomethylamine (MA) and monomethyl- d_3 -amine- d_2 (MAd_5) were run in the same model instrument using the same ionizing voltage by A. E. Williams of Petroleum Analytical Research Corporation, Houston, Texas. The data were analyzed by this writer making use of standard mass spectral tables¹⁴ and the redetermined mass spectra of the deuteromethanes.¹⁵ Due to air present (10-20%) in the mass spectrometer, it was impossible to determine the presence of CH_2D_2 ; therefore, all methane isotope analyses in the MA- MAd_5 series neglect CH_2D_2 .

The methane spectra were not corrected for the C^{13} isotope since error in the analysis of the methanes was greater (10%) than the correction. This large error was due to air present coupled with the small amounts of methane present. The error in the hydrogen isotope analysis was 1-2%. The spectra were not corrected for isotopic hydrogen impurity.

The four completely nondeuterated samples were analyzed by Gollob Analytical Service, Berkeley Heights, New Jersey. A Consolidated Electrodynamics Corporation Model 21-620A instrument was used employing an ionizing voltage of 70 volts.

RESULTS

The gamma radiolysis of monomethylamine was studied at ambient temperatures and constant total dose within a given series of experimental runs.

Products not previously reported for the radiolysis were found by use of the mass spectrometer in the analyses of both non-condensable* and condensable fractions of the irradiated gas. Ethane, nitrogen, trimethylamine, C₄ amine, and C₅ amine (specific compounds were not determined) are the newly detected products; they are all a small fraction of the major products (hydrogen, ammonia, methane, and dimethylamine) reported in this work and in earlier work.¹ Neither azomethane, ethylenimine, nor a polymer was detected as in the more recent photochemical study.⁷

Table 1 gives the experimental conditions for the irradiations. Tables 2 and 3 show the results of mass spectrometer analyses on experimental runs. Tables 4 and 5 illustrate the results of isotopic analyses obtained from the mass spectra for hydrogen and methane produced from the radiolysis of the dideutero compound and mixtures of non-deuterated and completely deuterated monomethylamine. These results reflect the 5% isotopic impurity (CH₃NDH) in the dideutero species and in the completely deuterated compound (CHD₂NDH).

A. Isotopic Hydrogen Analysis

In the radiolysis of monomethylamine-d₂, H₂, HD and D₂ were detected, the H₂/HD ratio is approximately 2 with D₂ being about one tenth of the HD. These results are consistent

* Those gases not condensable at -160°C are designated non-condensable.

Table 1

Radiolysis Samples

<u>Sample No.</u>	<u>Initial moles x 10⁵ methylamine</u>	<u>Initial Pressure (atm.)</u>	<u>Total Dose x10⁻¹⁸ (ev)</u>
MA-2	17.9	1.00	7.45
MA-3	27.5	1.49	7.25
MA-4	39.5	2.30	7.35
MA-Ar-71*	28.1	1.72	7.45
MA-14A	17.5	1.03	8.32
MAd ₂ -15A	27.4	1.52	8.50
MAd ₂ -15	28.0	2.13	8.40
MAd ₂ -16	40.8	2.15	8.50
MAd ₂ -Ar-51*	39.4	2.35	8.51

* — 3.1×10^{-5} moles of Argon added

MA = monomethylamine

MAd₂ = monomethylamine-d₂

continued-

Table 1 continued -

<u>Sample No.</u>	<u>Initial moles x 10⁵ methylamine</u>	<u>Initial Pressure (atm.)</u>	<u>Total Dose x10⁻¹⁸ (ev)</u>
MA-MAd ₅ -31A	MA -11.1 MAd ₅ -11.1	1.20	11.7
MA-MAd ₅ -51A	MA -17.3 MAd ₅ -16.4	1.99	11.5
MA-MAd ₅ -61A	MA -21.5 MAd ₅ -21.9	2.08	11.7
MA-MAd ₅ -101	MA - 5.8 MAd ₅ -10.9	0.98	9.6
MA-MAd ₅ -111A	MA -17.4 MAd ₅ -11.0	1.60	10.6
MA-MAd ₅ -121A	MA -27.2 MAd ₅ -10.8	2.21	11.0
MA-MAd ₅ -131	MA -39.4 MAd ₅ -11.2	2.64	11.4

MA = monomethylamine

MAd₅ = monomethyl-d₃-amine-d₂

Table 2

Mass Spectral Analyses of Products (Vol.%)

Sample No.	Non-Condensable Fraction				Condensable Fraction					
	<u>H₂</u>	<u>CH₄</u>	<u>C₂H₆</u>	<u>N₂</u>	<u>CH₃NH₂</u>	<u>NH₃</u>	<u>(CH₃)₂NH</u>	<u>(CH₃)₃N</u>	<u>C₄ amine</u>	<u>C₅ amine</u>
MA-2	94.0	3.7	0.1	0.4	85.0	14.0	0.5	0.06	0.02	< 0.01
MA-3	95.3	3.9	0.2	0.3	-	-	-	-	-	-
MA-4	95.2	3.4	0.2	0.2	49.0	50.6	0.4	0.08	0.02	0.01
MA-Ar-71	94.3	5.3	0.4	N.D.	-	-	-	-	-	-

N.D. = not detected

— = not analyzed

Table 3

Mass Spectral Analyses of Products (Vol.%)

<u>Sample No.</u>	<u>H₂</u>	<u>CH₄</u>	<u>Sample No.</u>	<u>H₂</u>	<u>CH₄</u>
MAd ₂ -14A	97.5	2.5	MA-MAd ₅ -31A	95.0	5.0
MAd ₂ -15A	97.0	3.0	MA-MAd ₅ -51A	96.1	3.9
MAd ₂ -15	96.9	3.1	MA-MAd ₅ -61A	95.8	4.2
MAd ₂ -16	96.8	3.2	MA-MAd ₅ -101	95.4	4.6
MAd ₂ -Ar-51	96.3	3.7	MA-MAd ₅ -111A	95.2	4.8
			MA-MAd ₅ -121A	95.5	4.5
			MA-MAd ₅ -131	96.1	3.9

Note: C₂H₆ and N₂ were not taken into consideration in the analyses.

Table 4

Isotopic Analyses of the Non-Condensable Fractions
from CH_3ND_2 (%)

<u>Sample No.</u>	<u>Hydrogen</u>			<u>Methane*</u>	
	<u>H₂</u>	<u>HD</u>	<u>D₂</u>	<u>CH₄</u>	<u>CH₃D</u>
MAd ₂ -14A	65.7	30.5	3.8	68	32
MAd ₂ -15A	66.4	30.6	3.0	80	20
MAd ₂ -15	65.5	31.0	3.5	80	20
MAd ₂ -16	70.4	26.8	2.8	82	18
MAd ₂ -Ar-51	68.0	29.1	2.9	100	N.D.

* No other forms of isotopic methane detected

N.D. - not detected

Table 5

Isotopic Analyses of Hydrogen and Methane from $\text{CH}_3\text{NH}_2\text{-CD}_3\text{ND}_2$ (%)

<u>Sample No.</u>	<u>Hydrogen</u>			<u>Methane*</u>			
	<u>H₂</u>	<u>HD</u>	<u>D₂</u>	<u>CH₄</u>	<u>CH₃D</u>	<u>CD₃H</u>	<u>CD₄</u>
MA-MAd ₅ -31A	58.5	32.6	8.9	23	38	31	8
MA-MAd ₅ -51A	63.2	29.6	10.2	22	40	30	8
MA-MAd ₅ -61A	59.4	32.0	8.6	23	41	28	8
MA-MAd ₅ -101	47.5	40.8	11.7	18	27	46	9
MA-MAd ₅ -111A	66.3	25.8	7.9	40	25	26	9
MA-MAd ₅ -121A	76.1	19.9	4.2	45	25	22	8
MA-MAd ₅ -131	80.7	17.0	2.6	57	19	17	7

* CH_2D_2 not determined

over a 2.3 fold increase in initial number of moles and a 2-fold increase in initial pressure. The total dose was essentially held constant. There is no significant change in the results from the sample containing added argon.

Two series of mixtures of monomethylamine and monomethyl-d₃-amine-d₂ were studied. One of the series (MA-MAd₅-31A through 61A) consisted of an equal mole mixture. In the other (MA-MAd₅-101 through 131), the number of moles of the completely deuterated amine was held constant and the number of moles of the nondeuterated compound was varied from one half to more than three times (a 6-fold increase in MA) that of the deuterated amine (see Table 1).

The analysis of the equal mole mixture shows the major components of hydrogen to be H₂ and HD in the ratio of roughly 2 to 1, with D₂ slightly greater than one third of HD. The results are consistent over a 2-fold increase in initial number of moles and slightly less than a 2-fold increase in initial pressure; the total dose was held constant.

In the varying mole series, the relative amounts of H₂, HD, and D₂ vary from a ratio of 4:4:1, at the lowest number of moles of initial undeuterated amine, to a ratio of 40:10:1, at the highest number of moles. The results of sample MA-MAd₅-31A (equal mole series) fit well into the general trend of the varying series as would be expected from the initial conditions of MA-MAd₅-31A. This trend is over a 2.7 fold increase in initial pressure with a 15% variation of dose in one sample, MA-MAd₅-101.

Comparisons of various hydrogen isotope ratios are given in Tables 6 and 7.

B. Isotopic Methane Analysis

The radiation methane products of the dideutero amine are CH₄ and CH₃D, there is no indication of CH₂D₂ present.

Table 6
Comparison of Isotopic Analyses
(CH₃ND₂ System)

<u>Sample No.</u>	<u>H₂/HD</u>	<u>H₂/D₂</u>	<u>HD/ D₂</u>	<u>CH₄/CH₃D</u>
MAd ₂ -14A	2.2	17	8.0	2.1
MAd ₂ -15A	2.2	22	10	4.0
MAd ₂ -15	2.1	19	8.9	4.0
MAd ₂ -16A	2.6	25	9.5	4.5
MAd ₂ -Ar-51	2.4	24	10	-

Table 7

Comparison of Isotopic Analyses
($\text{CH}_3\text{NH}_2\text{-CD}_3\text{ND}_2$ mixture)

Sample No.	$\frac{\text{MA}}{\text{MAd}_5}$	$\frac{\text{H}_2}{\text{HD}}$	$\frac{\text{H}_2}{\text{D}_2}$	$\frac{\text{HD}}{\text{D}_2}$	$\frac{\text{CH}_4}{\text{CH}_3\text{D}}$	$\frac{\text{CH}_3\text{D}}{\text{CD}_3\text{H}}$	$\frac{\text{CH}_4}{\text{CD}_4}$
MA-MAd ₅ -31A	1.0	1.8	6.6	3.7	0.61	1.2	2.9
MA-MAd ₅ -51A	1.1	2.1	6.2	3.0	0.55	1.3	2.7
MA-MAd ₅ -61A	0.98	1.9	6.9	3.8	0.56	1.5	2.9
MA-MAd ₅ -101	0.53	1.2	4.1	3.5	0.67	0.59	2.0
MA-MAd ₅ -111A	1.6	2.6	8.4	3.3	1.6	0.96	4.4
MA-MAd ₅ -121A	2.5	3.8	18	4.6	1.8	1.1	5.6
MA-MAd ₅ -131	3.5	4.7	31	6.5	3.0	1.1	8.2

CH_3D and CD_3H are the major methanes in the radiation of the $\text{CH}_3\text{NH}_2\text{-CD}_3\text{ND}_2$ equal mole mixture series.

The relative amounts of CH_4 , CH_3D , CD_3H show a trend consistent with the $\text{CH}_3\text{NH}_2\text{-CD}_3\text{ND}_2$ ratio. CD_3H is the major component at the low CH_3NH_2 concentration while CH_4 is predominant at the high CH_3NH_2 concentration.

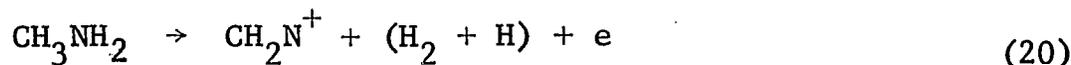
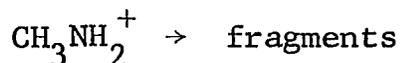
Comparisons of various ratios of isotopic methanes are given in Tables 6 and 7. Because of the error involved in the isotope analysis, these values can be only taken as approximations or to indicate a trend.

DISCUSSION

The purpose of this work is to elucidate, with the aid of isotopic analysis of the hydrogen and methane produced, the primary process, or processes, involved in hydrogen and methane production in the gamma radiolysis of monomethylamine.

The electromagnetic radiation of cobalt-60 (1.17 and 1.33 Mev) gives up energy to the methylamine through secondary electrons produced by the Compton effect. The Compton effect is an elastic collision between a photon and a single electron, usually at the wall of the container in this case. The incident photon gives up a portion of its energy to the electron and a photon of lower energy is emitted. The Compton electron having an energy spectrum of 0 to 1.04 Mev., interacts with the system producing ionization and excitation.

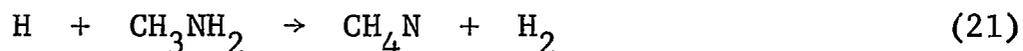
The following possible primary dissociations of gaseous monomethylamine may be considered.



Reaction (16) is presented as an example of intramolecular formation of hydrogen, similar to the reactions discussed in

the work of Dorfman² and Okabe³ on the ethane system. The fragment CH_3N might have any one of the forms: CH_2NH , CH_3N , CHNH_2 . The relationships in (18), (19), and (20) are associated with the major peaks of monomethylamine observed in a mass spectrometer.¹⁴ It is worthwhile to consider these reactions since there has been some success in predicting yields and products of radiation studies observed from the mass spectrometer spectral pattern.¹⁶ Recently, Stief and Ausloos⁴ have applied this type of analogy successfully in studies of the gamma radiolysis of CH_3CD_3 . Reactions (18) and (20) could be quite significant compared to reaction (19) since in the mass spectra, with the peak intensity at mass 30 taken as 100, the peak intensities at mass 31 and mass 28 are 56 and 88, respectively. The fragments CH_4N^+ and CH_2N^+ have not been characterized.¹⁷

The track concept disappears in the gaseous state, therefore, reaction of any hydrogen atom with the substrate would take place with a greater probability than with another hydrogen atom to yield the hydrogen molecule.

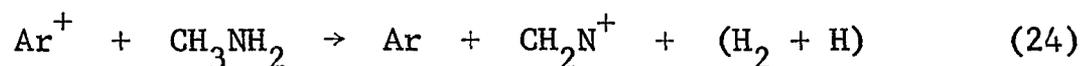
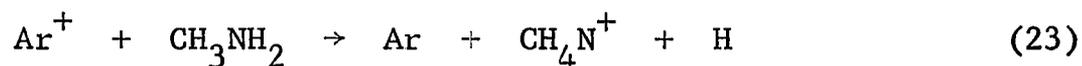
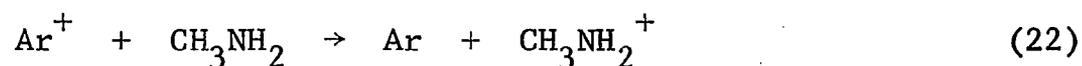


Subsequent reaction of the ions in (18), (19), and (20) could lead to various molecular species.

Inspection of Table 3 indicates that H_2 is the most abundant hydrogen formed in the radiolysis of CH_3ND_2 . This result differs markedly from those of the more recent study⁷ of the photolysis of CH_3ND_2 where analysis of the hydrogen yielded H_2 - 16%, HD - 81%, D_2 - 3% compared to H_2 - 67%, HD - 30%, D_2 - 3% from this work. The photochemical study was conducted at 141 mm. Hg pressure. In both this present study and the previous one¹ in radiolysis there is no indication of fluctuation in total hydrogen production or variation in

isotopic distribution, within experimental error, corresponding to a change in pressure. Addition of 7.3 mole percent argon (ionization potential, Ar = 15.8 eV¹⁸, CH₃NH₂ = 8.97 - 9.41 eV^{18,19}) apparently has no effect.

Reactions (18) through (20) cannot be considered important in hydrogen production since neither total hydrogen yield nor relative abundance of the isotopic forms of hydrogen change on addition of argon. Reactions



should be operative²⁰ and enhance total hydrogen production. Reaction (24) may have an effect on isotopic distribution.

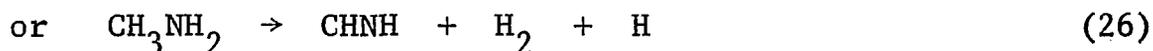
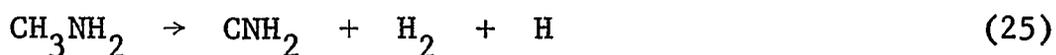
If reaction (16) were of major consequence, a larger quantity of HD (approximately 60%) would be expected from the CH₃ND₂. In the CH₃NH₂-CD₃ND₂ equal mole series negligible amounts of HD should result. Neither are in agreement with experiment. The above results are based on the theory that the carbon and nitrogen both furnish a hydrogen atom (binuclear intramolecularity*). If molecular hydrogen is formed from carbon alone and from nitrogen alone (mononuclear intramolecularity), H₂ and D₂ should be the major constituents in both series. Table 3 and Table 4 do not indicate this to be the case.

The question of whether carbon and nitrogen are equally effective in furnishing hydrogen, either atomic or

* Although the term "intramolecularity" does not appear in Webster's dictionary, it is used here for clarity.

molecular, has not been resolved. Brinton²¹, in a study of methyl radical abstraction of hydrogen from various amines at 156°C, shows a lability of the hydrogen on nitrogen in compounds such as dimethyl- and diethylamine. Brinton further states that the evidence does not support nor contradict this in monomethyl- and monoethylamine and both the hydrogen on the carbon and the hydrogen on the nitrogen may be active. Kozak and Gesser²², in a similar work, indicate the lability to be with the hydrogen on the carbon in diethylamine. Trotman-Dickinson and Steacie²³ interpret the results of a study of abstraction of hydrogen from monomethylamine by methyl radicals, between 186-347°C, to indicate three active hydrogens, these presumably being on the carbon.

To apply the lability effect to intramolecular hydrogen elimination may be speculative, although reaction (20) and its weight factor in the mass spectra support the importance of the labile hydrogen. This would be especially pertinent if the fragment $(\text{CH}_2\text{N})^+$ is found to be CNH_2^+ . Eliminating the possibility of ion formation may still lead to the postulate that



may be important reactions. These are cases of both intramolecular formation of hydrogen and potential intermolecular formation of hydrogen. If reaction (25) were important, the product hydrogen from CH_3ND_2 should show principally H_2 with little or no HD or D_2 . The reason for the expected absence of HD and D_2 is due to the absence of contribution from nitrogen in either molecular hydrogen or atomic hydrogen. The results from equal mole mixtures of $\text{CH}_3\text{NH}_2\text{-CD}_3\text{ND}_2$ should indicate approximately equal amounts of H_2 and D_2 with smaller

amounts of HD. Tables 4 and 5 do not verify these expectations.

With reaction (26), the CH_3ND_2 series should reflect principally HD. Table 4 does not enforce this expectation.

Assuming the hydrogen on the nitrogen to be active along with the lability effect may lead to expected results in the CH_3ND_2 system that would be in agreement with experimental values, if the molecular hydrogen is formed by binuclear intramolecularity. This would not be the case if the molecular species arose from mononuclear intramolecularity in CH_3ND_2 . In either case the experimental data from the CH_3NH_2 - CD_3ND_2 equal mole series show too high a content of HD relative to H_2 and D_2 for the mechanisms to be of major consequence.

Another effect that must be considered is the isotope effect. This phenomenon has been encountered by Stief and Ausloos⁴ in a study of the radiolysis of CH_3CD_3 ; an isotope effect of 1.7 in favor of H_2 formation over D_2 formation was found. Dorfman², working on the radiolysis of C_2H_6 - C_2D_6 equal mole mixtures, noted a 1.5 factor favoring H_2 production. Okabe and McNesby³, investigating the photolysis of CH_3CD_3 , showed an isotope effect of slightly greater than 2. These workers all found large contributions due to intramolecular formation of hydrogen.

Invoking the isotope effect in mononuclear intramolecularity in the CH_3ND_2 system leads to anticipated yields showing a high yield of H_2 and D_2 in some fixed ratio and relatively small amounts of HD. This is not the experimental case (Table 4). Using binuclear intramolecularity under the same conditions may lead to a rationalized agreement in expected and experimental results for the CH_3ND_2 although the empirical value of H_2 may be too high. In the CH_3NH_2 - CD_3ND_2 system the observed value of HD is too high to make the result

meaningful in terms of binuclear intramolecular formation of hydrogen.

A combination of the lability effect and the isotope effect coupled with intramolecular elimination of molecular hydrogen cannot explain the relatively high HD percentage in the product hydrogen from the equal mole $\text{CH}_3\text{NH}_2\text{-CD}_3\text{ND}_2$ series.

The data appear not to support reactions (16), (25) and (26) as major contributors to the primary dissociation process.

Reaction (17) is given in regard to methane formation and will be treated later in the text.

The evidence must now be considered in light of reactions (14) and (15). The decision of selecting one reaction over the other is a difficult one. Using thermodynamic data²⁴ on the standard molar heat of formation of monomethylamine and the hydrogen atom and taking bond energies of C-H and N-H²⁵ to be bond dissociation energies used as standard molar heats of reaction does not help elucidate the choice. The manipulation gives the standard molar heat of formation for $\text{CH}_3\text{NH} = 36.2 \text{ kcal. mole}^{-1}$ and for CH_2NH_2 a value of $42.2 \text{ kcal. mole}^{-1}$. Since the equating of bond energy and bond dissociation energy is not strictly allowed in this case, the calculations give only a rough approximation and show that the heats of formation are quite close, making a choice of one reaction in favor of the other difficult.

Assuming elimination of hydrogen atom from the excited monomethylamine molecule followed by subsequent reaction of the atom with the substrate, the expected yield of hydrogen products is $\text{H}_2 - 36.0\%$, $\text{HD} - 48.0\%$ and $\text{D}_2 - 16.0\%$. The figures are based on a random distribution of H and D consistent with the molecule. Any atom-atom reactions are ignored since track effects are considered negligible in the vapor state. These

findings are not in agreement with the experimental results.

An isotope effect has been found in both radiolysis and photolysis studies when intramolecular detachment of hydrogen is considered of great importance. It is also known that in the dissociation of gaseous chloroform²⁶ in a mass spectrometer an isotope effect of approximately 3 in favor of H elimination over that of D in the deuterio compound exists. Eyring and Cagle²⁷ have calculated the ratio of specific rate constants of the hydrogen and deuterium compound for the above system using the fundamental stretching frequencies of the C-H and C-D bond in the different species. The calculations showed a factor of 2.89 in favor of H. Employing the same approach* and the values of the C-H and N-D fundamental stretching frequencies of CH_3ND_2 from Gray and Lord⁸ results

$$* \frac{k_{\text{H}}}{k_{\text{D}}} = \exp \left\{ \frac{hc}{2kT} (\bar{\nu}_{\text{H}} - \bar{\nu}_{\text{D}}) \right\}$$

$k_{\text{H}}, k_{\text{D}}$ = specific rate constant

c = velocity of light

k = Boltzmann constant

h = Planck's constant

T = absolute temperature (298°K)

$\bar{\nu}$ = wave number of the bond linking hydrogen to another atom, this bond is cleaved in the reaction

It is assumed that the partition function of all degrees of freedom, except for reaction coordinate, cancel out. The reaction coordinate is the bond involving hydrogen abstraction by hydrogen atom.

in k_H/k_D equal to approximately 2.7. Because of the nature of the interaction²⁸ of high energy (Compton) electrons with the system, it is not thought that the isotope effect would be connected with the initial elimination of the hydrogen or deuterium atom from the excited molecule, but may occur in the atom-substrate molecule reaction in the formation of molecular hydrogen at near thermal energies. Applying the calculated value to simple probability calculations, where now the probability of D abstraction is $2/5 \times 1/3.7$ and the probability of H abstraction is $1 - (2/5 \times 1/3.7)$, the expected values are H_2 - 55%, HD - 42%, D_2 - 3%. When the isotopic impurity on the nitrogen is considered, the values are H_2 - 56%, HD - 40%, D_2 - 4%, compared to the observed H_2 - 67%, HD - 30%, D_2 - 3% (Table 3).

The isotope effect should also be reflected in the H_2/D_2 ratio of the CH_3NH_2 - CD_3ND_2 equal mole series. Calculations indicate that the isotope effect on the carbon should be 6.2 and on the nitrogen 7.1; therefore, the H_2/D_2 ratio in the equal mole series should fall between the limits of 6.0 and 7.3. Table 7 gives the ratio 6.6.

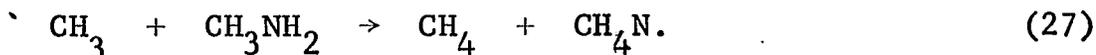
The data definitely suggest intermolecular formation of hydrogen as the major primary process.

A possible explanation for the shift in favor of H_2 in the experimental results may be preferred mononuclear intramolecular elimination of molecular hydrogen. This has been found to be true by Okabe and Stief^{3,4} with CH_3CD_3 . With this second mechanism operating, the H_2 and D_2 content would be increased while effectively lowering HD in the CH_3ND_2 series. Invoking a 15% intramolecular effect leads to expected values of H_2 - 65%, HD - 31% and D_2 - 4%. The two mechanisms are considered operative at the same time, yet independent of one another.

A problem arises when the results dealing with the isotope effect on mononuclear intramolecularity are considered. The isotope effect that has been demonstrated^{3,4} may mean it is operative in the excited bonds of the molecule. If this is the case, the excited isotope effect could account for the observed results when the intermolecular mechanism is the only contributor to the primary process. Since the actual mechanism of mononuclear intramolecular elimination of hydrogen is not understood, the two-mechanism approach may be tentatively considered the more reasonable rationalization.

Simple probability calculations, that consider the two-mechanism approach and the isotope impurity of the deuterio compound, with the equal mole $\text{CH}_3\text{NH}_2\text{-CD}_3\text{ND}_2$ series yield results of H_2 - 56%, HD - 40%, and D_2 - 4%. These figures are in reasonable agreement with the observed ones (Table 4); the calculations consider every collision effective.

The amount of methane formed is only 4% of the hydrogen in the non-condensable fraction from the radiolysis of monomethylamine. In the CH_3ND_2 the only methanes detected were CH_4 and CH_3D (Table 3). This would suggest a reaction such as (17) followed by



Another possible reaction is



The absence of CH_3D in sample $\text{MAd}_2\text{-Ar-51}$ is not well understood in light of the fact that total methane production is not appreciably changed with addition of argon in samples MA-Ar-71 and MA-Ar-51 (Tables 2 and 3). More work should be

done on this system. Reactions

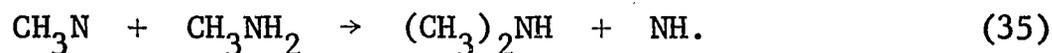
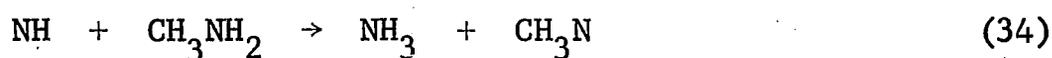
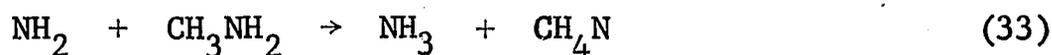


could be important. The mass-charge ratio peak intensities of NH_2^+ and CH_3^+ in methylamine show an abundance of 10-15%.²⁹ The evidence (Table 2) does not support these reactions. Because of the lack of information on the presence of CH_2D_2 in the equal mole series, the data do not lend themselves to interpretation especially in view of the error involved in analysis. The results of the CH_3ND_2 clearly indicate that two possible mechanisms in methane production must be considered, reactions (17) and (28). Assuming that (17) is operative, the data show an isotope effect of 4 in favor of hydrogen. This is purely speculative since there is no way of deciding between the two mechanisms.

An interesting point is raised in consideration of the carbon-nitrogen bond rupture. Comparing the strength of the C-N bond in CH_3NH_2 ⁵ (80 kcal.) relative to the strength of the C-H bond²⁵ (approximately 100 kcal.) or the N-H bond²⁵ (approximately 95 kcal.) may lead to the conclusion that more products should be produced by C-N bond scission than by C-H or N-H bond scission. This is not the case in the gamma radiolysis of ethane^{2,4} (C-C bond strength = 82 kcal.), the photolysis of ethane³, the photolysis of methylamine⁷, or the reaction of recoil tritium atoms with ethane.³⁰ The reason noted by Urch and Wolfgang³⁰, may be that the C-H and N-H bonds are more exposed than the C-N bond. This does not rule out energetics completely as seen by the isotope effect encountered in the radiolysis and photolysis of ethane.

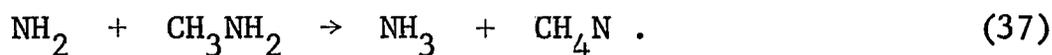
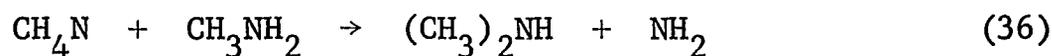
With reaction (17) operative, the NH_2 fragment may

act as an initiator in reactions such as

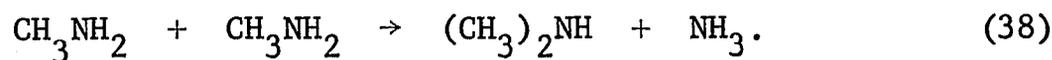


Reaction (17) alone cannot account for the yield of ammonia.¹

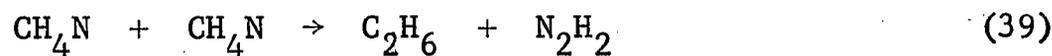
The CH_4N fragment of reaction (14) and (15) can also lead to ammonia



The CH_3N fragment from the intramolecular path may react as shown in reaction (35). Radicals may very well account for some of the production of ammonia; a 22% decrease has been noted¹ on addition of iodine. Dimethylamine has been found to undergo an initial build up in concentration followed by a decrease with irradiation time¹; it would be subject to the same fate in the above. Another path for ammonia production is

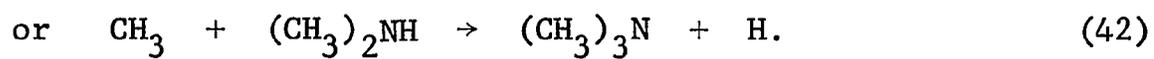
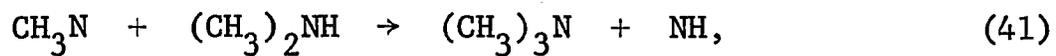


Production of ethane and nitrogen can be rationalized by



Hydrazine has been postulated to be the precursor in nitrogen production in the photolysis of ammonia³¹ but the mechanism of its formation is not well understood. The above path may be plausible since enough CH_4N fragments should be present.

The triethylamine could be accounted for by



The mechanism for the production of C₄ and C₅ amine probably involves a free radical, but to characterize the paths is difficult since the structures are not known.

SUMMARY

The gamma radiolysis of monomethylamine, monomethylamine-d₂, and mixtures of monomethylamine and monomethyl-d₃-amine-d₂ was studied at ambient temperatures. Products not previously reported were found by mass spectrometry to be ethane, nitrogen, trimethylamine, C₄ amine, and C₅ amine. These products are all small fractions of the major products: hydrogen, ammonia and methane.

Isotopic analysis of the hydrogen product definitely indicates a two mechanism production of molecular hydrogen. The major contributor to the primary process in hydrogen formation is elimination of hydrogen atom from the excited molecule followed by subsequent reaction of hydrogen atom with the substrate.

A contribution of 10-15% is attributed to mononuclear elimination of molecular hydrogen.

Methane formation can be accounted for by either methyl radical production or intramolecular formation of methane.

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